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TEMPER EMBRITTLEMENT OF 2 1/4Cr-1Mo STEEL

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by

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1. INTRODUCTION

Steels containing chromium and molybdenum have received wide application in the petrochemical industry (1). In particular, the 2 1/4% Cr - 1% Mo alloy is used in heavy-wall pressure vessels (2) because of its good combination of deep hardenability to bainitic or auto-tempered martensitic micro-structures, resistance to creep and hydrogen attack, and resistance to temper embrittlement. A forthcoming review will summarize these characteristics (3). The objective of the present report is to review the state-of-the-art regarding the understanding and control of temper embrittlement in 2 1/4% Cr - 1% Mo steels.

During fabrication of structures from 2 1/4% Cr - 1% Mo steels, heat treatment in the vicinity of 675°C is commonly used (4) either for tempering or post-weld heat treatment. During cooling from this temperature, or during service at temperatures between 350 and 575°C, a loss in toughness may occur. This is the phenomenon of temper embrittlement (TE), in this case termed "two-step" or "reversible" TE to distinguish it from the "one-step" or "tempered Martensite" embrittlement, that can occur in the vicinity of 350°C (5) during the tempering of quenched-alloy steels.

It has been known for many years that the second form of TE is promoted by the presence of impurity elements (6) which concentrate at grain boundaries, thus, weakening them. This process has become much better understood with the aid of Auger electron spectroscopy (7-14). Of special interest in Cr/Mo steels is the role of Mo in retarding embrittlement, and the question of whether Mo retains its effectiveness during prolonged service at temperatures in the embrittlement range. Accompanying this improved understanding of the microstructural causes of temper embrittlement is an increasing interest in using the quantitative methods of fracture mechanics to characterize the toughness of embrittled microstructures.

2. TEST TECHNIQUES

Temper embrittlement has no effect on the yield strength, but impairs fracture resistance by providing a low-energy crack path along grain boundaries enriched with deleterious impurities such as P during the tempering treatment. Conventionally, this effect is studied using the Charpy V-notch impact test, by measuring the shift in ductile/brittle transition temperature as a function of tempering treatment. A step-cooling heat treatment is often used to provide a greater degree of embrittlement than can be produced during a practical time (several months or less) by isothermal treatment.

The loss of toughness is directly attributable to changes in grain boundary composition, which can now be measured directly by Auger analysis of intergranular fracture surfaces. The composition-dependent loss in cohesion should be reflected in a decrease in energy of fracture. However, there is no direct relation of this quantity to a Charpy energy. Charpy data are useful in a comparative sense, but cannot be used in design and are very diffi-

cult to interpret fundamentally. It would be desirable, in view of the advances that have been made in quantitative measurement of grain boundary chemistry, to have a complementary advance in measurement of the mechanical parameters of fracture.

Fundamentally-based fracture parameters have been developed by the methods of fracture mechanics. Linear-elastic fracture mechanics (LEFM) has allowed rational development of design criteria for high-strength materials, and current work on yielding fracture mechanics (YFM) shows promise in extending these methods to lower-strength, tougher materials (15). Combinations of LEFM and YFM methods have been used to characterize the toughness of 2 1/4% Cr - 1% Mo steels (16,17). It has been demonstrated (17) that static K_{Ic} values can be predicted quite accurately from dynamic Charpy results; this development indicates that changes in Charpy transition temperature are likely to be accompanied by changes in static fracture toughness. It is therefore desirable, and to be expected, that TE will be characterized in future work by changes in fracture mechanics parameters such as K_{Ic} and K_{Id}.

3. EFFECTS OF COMPOSITION, TEMPERATURE, TIME, AND MICROSTRUCTURE ON EMBRITTLEMENT of 2 1/4% Cr - 1% Mo STEEL

It is now well established that TE occurs because impurity elements segregate to grain boundaries and result in a loss in grain boundary cohesion. The effect is enhanced by certain alloy elements which in some cases segregate to grain boundaries and increase the impurity level there through attractive interactions, or in other cases promote segregation by repulsive interactions with impurity elements in the body of the grain.

Chromium/molybdenum steels exhibit the full complexity of these effects. Temper embrittlement in 2 1/4% Cr - 1% Mo steels has been reviewed recently (18), and further advances in understanding have been made since the review appeared. Ductile/brittle transition temperatures of commercial grades of these steels may increase by more than 100°C after several years of service (19). Figure 1 summarizes the known actions of alloy and impurity elements in alloy steels, and a representative analysis of commercial grades of 2 1/4% Cr - 1% Mo steels is given in Table 1. Embrittlement by P, Sn, Sb, and As is expected, and will be assisted by Mn, Cr, and Ni. The roles of Mo and Si are rather special, as elaborated in recent work (20,21) and described later in this section.

The net loss in grain boundary cohesion is proportional to the grain boundary concentration of embrittling elements weighted by their relative potency in reducing the strength of the boundary per unit concentration of embrittling element. This concentration is due to co-segregation with alloy elements and proportional to the activity of the embrittlement agent in the bulk. For example, S is not deleterious in these steels because it is scavenged by Mn, reducing its activity to near zero. Consistent with this synergism, it might be expected that an "embrittlement factor" such as (Mn + Ni + Cr + Si) x (P + Sn + Sb + As) would be useful to indicate TE susceptibility, and various empirical formulas of this type have appeared in the literature. Bruscato (22) suggested that TE susceptibility in 2 1/4% Cr - 1% Mo steels was related to the Mn + Si content and the P + Sn impurity level. Researchers at the Japan Steel Works have recently quantified this suggestion (23) as the "J-factor" $(Mn + Si)(P + Sn) \times 10^4$ which is quite successful in predicting the maximum TE susceptibility in 2 1/4% Cr - 1% Mo steels. While recognizing the empirical usefulness of such a factor, it must be borne in mind that unusually high levels of elements such as Ni or Sb could cause signifi-

cant degradation beyond that given by the J-factor. Recent work (20,21) has indicated that in these steels the principal embrittling agent is P and that Sn has little effect, being scavenged by Mo, at least up to 0.04% Sn. Manganese acts as a co-segregant with P, and Si appears to increase the P activity by a bulk repulsive interaction. Molybdenum has its principal effect on the kinetics of segregation; it should be noted that Mo is beneficial up to 0.7% Mo (24), but beyond this level it increases TE susceptibility, presumably by a grain boundary co-segregation mechanism or possibly by increasing hardness (24).

Although the presence of Mo alters the kinetics of segregation and reduces the embrittlement produced by step cooling, it has little effect on ultimate levels of embrittlement after long exposure. It is now well established that a conventional step-cooling embrittlement treatment does not produce the maximum possible embrittlement, and that exposure for several years in the range 350 to 450°C can cause increases in transition temperature up to three times as large as those resulting from step cooling (19). This is most likely a result of the transient effects of Mo on the activity of P. Molybdenum ties up P during the initial stages of aging, but in the later stages releases this P as the Mo reacts with C to form more stable carbides. Temper embrittlement in Cr/Mo alloys is therefore characterized by a rapid stage following $\sqrt{Dt}$ kinetics (26) as the untrapped P diffuses to the grain boundaries, followed by a gradual rise in the P concentration as it is released from transient trapping by Mo and becomes available for diffusion.

The transformation characteristics of 2 1/4% Cr - 1% Mo steel are such that upper bainite is formed as a result of commercial normalizing or accelerated cooling of heavy sections. Consequently, it is the TE of this microstructure that is primarily of interest. Prior austenite grain size has a significant effect on TE, the susceptibility increasing with increasing

grain size. Although the detailed mechanism of this effect remains to be established, the reduced toughness of the coarse-grained material correlates with an increasing proportion of intergranular fracture (26).

The properties of weld metal and HAZ of 2 1/4% Cr - 1% Mo after exposure are obviously important, as there is no reason to suppose that these regions are less susceptible to TE than the base plate. Bruscato (22) studied weld deposits using shielded metal-arc electrodes conforming to ASTM A316, and found the TE response broadly similar to that of the base metal. More recently, Copeland and Yuen (27) have introduced fracture mechanics methods for the study of welds in the post-weld heat-treated condition. They found that the HAZ had low toughness at elevated temperatures (~500°C) although the effect of TE on the weld metal and HAZ was not reported.

4. EMBRITTLEMENT-RESISTANT ALLOYS

In some applications, TE can be minimized by simply avoiding long exposure in the embrittling temperature range. This remedy is not available, of course, for structures that are required to operate for long times in this range, which is commonly the case where 2 1/4% Cr - 1% Mo steels are used.

Another obvious remedy is composition control, either of tne alloy elements that ennance TE or of the embrittling impurities themselves. However, there are obvious limits to which the concentration of useful alloy elements can be reduced. Chromium and Mo are needed for control of transformation, to form stable carbides for creep strength and prevention of hydrogen attack, and, in the case of Cr, for oxidation resistance as well. Manganese is needed to scavenge S, and at least in the weld metal cannot be reduced below 0.5% without serious loss in toughness (22). Of the major alloy additions, this leaves only Si. It has been proposed (28) that Si be

reduced to very low levels by the use of vacuum carbon deoxidation (VCD), using C rather than Si as a deoxidant. This appears to be a practical solution, at least for base material. Weldability of low-silicon electrodes would have to be evaluated.

Trace impurity levels can be reduced only at considerable cost. However, the effective concentration of embrittling impurities can be minimized by the addition of scavenging elements, e.g., the effect of Mn on S. Rare earths have been used for this purpose, although not very successfully (29). A much improved theory is now available (30) to enable the required amounts of scavengers to be estimated. Seah et al (31) have shown that TE of 2 1/4% Cr - 1% Mo steel may be minimized by the addition of a suitable amount of mischmetal. This appears to be a promising remedy, although effects on welding and on toughness remain to be established.

SUMMARY

Significant toughness loss can occur by TE of 2 1/4% - 1% Mo steels, an upward shift in transition temperature of more than 100°C having been found after several years' exposure in the embrittling temperature range. Temper embrittlement can occur in both base metal and weld metal, and almost certainly in the HAZ as well, although this region has not been extensively studied.

Of possible remedies for TE, the most practical ones appear at present to be the reduction of Si levels in the base metal, and addition of rare earth elements in the weld electrodes. These remedies remain to be confirmed through further experimental work. Their effects on TE should be characterized by fracture mechanics parameters such as K_{1c} and K_{1d}.

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Table 1 - Representative analysis of 2 1/4% Cr - 1% Mo Commercial grades

	C	Mn	Cr	Mo	Si	Cu	Ni	S	N	P	Sn	Sb	As
Typical	0.14	0.4	2.25	1.0	0.3	0.2	0.2	0.02	0.01	0.01	0.02	0.004	0.02
A542 limits	0.15 max	$\frac{0.6}{0.3}$	$\frac{2.50}{2.25}$	$\frac{1.10}{0.90}$	0.50 max			0.035 max		0.035 max			

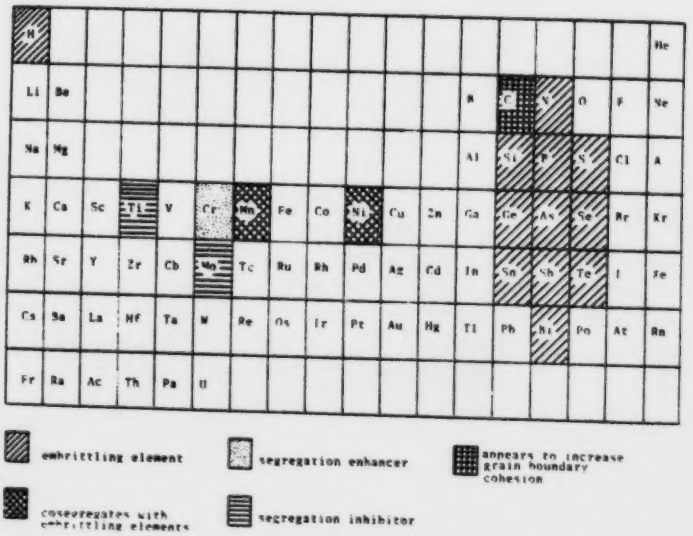

Fig. 1 - Effects of various elements on impurity induced embrittlement of steels. From ref (32) (neg 2362).